

Isotropic-Nematic Transition in Liquid-Crystalline Elastomers

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(Dated: September 24, 2002)

In liquid-crystalline elastomers, the nematic order parameter and the induced strain vary smoothly across the isotropic-nematic transition, without the expected first-order discontinuity. To investigate this smooth variation, we measure the strain as a function of temperature over a range of applied stress, for elastomers crosslinked in the nematic and isotropic phases, and analyze the results using a variation on Landau theory. This analysis shows that the smooth variation arises from quenched disorder in the elastomer, combined with the effects of applied stress and internal stress.

Liquid-crystalline elastomers are unusual materials that combine the elastic properties of rubbers with the anisotropy of liquid crystals [1, 2]. They consist of crosslinked networks of polymers with mesogenic units. Because of this structure, any stress on the polymer network influences the orientational order of the liquid crystal, and conversely, any change in the orientational order affects the shape of the elastomer. These materials are being actively studied for both basic research [3, 4, 5, 6, 7] and applications, including use as actuators or artificial muscles [8]. For this application, a change in temperature near the isotropic-nematic transition induces a large change in the orientational order, which causes the elastomer to extend or contract.

In this paper, we investigate the isotropic-nematic transition in liquid-crystalline elastomers. In conventional liquid crystals, this is a first-order transition, with a discontinuity in the magnitude of the orientational order as a function of temperature. By contrast, experiments on liquid-crystalline elastomers show that both the orientational order parameter and the elastomer strain change smoothly at this transition, with no first-order discontinuity [8, 9, 10, 11, 12]. Surprisingly, this is neither a first- nor a second-order transition, but rather a rapid nonsingular crossover from the isotropic to the nematic phase. Thus, the key question is how to explain this difference between conventional liquid crystals and liquid-crystalline elastomers. That question is important for basic research, because it shows how orientational ordering is affected by coupling to a crosslinked polymer network. That question is also important for applications, because it shows how to optimize these materials for artificial muscles, which should have the greatest possible length change for a fixed temperature change.

There are two possible explanations for a smooth crossover from the isotropic to the nematic phase. The first explanation is based on the effect of an aligning stress on a first-order transition [13]. The classical theory of phase transitions predicts the generic behavior shown in Fig. 1. For a stress below the critical point, a system has a first-order discontinuity in the order parameter at the transition. As the stress increases, the discontinuity decreases. When the stress reaches the critical point,

the discontinuity vanishes and the system has an infinite slope in the order parameter as a function of temperature. Beyond the critical point, the system evolves smoothly from the disordered to the ordered phase. In liquid-crystalline elastomers, an aligning stress may come from an applied stress on the sample. It may also come from an internal stress due to crosslinking an elastomer in the nematic phase, which imprints orientational order in the pattern of crosslinks. It is possible that the combination of applied stress and internal stress might put an elastomer beyond the critical point, so that it would show a supercritical evolution from the isotropic to the nematic phase. If this explanation is correct, then one would optimize elastomers for applications by working close to the critical point, where the slope is greatest.

An alternative explanation for this behavior is heterogeneity in an elastomer. The polymerization and crosslinking process induces some quenched disorder in a sample. For example, polydispersity in the chain length gives one type of disorder. This disorder may lead to a distribution of regions with different isotropic-nematic transition temperatures. In that case, at any given temperature, a sample would have a coexistence of isotropic and nematic domains. As the temperature decreases, it would cross over from mostly isotropic to mostly nematic, leading to a smooth evolution in the average orientational order parameter and in the macroscopic strain. If this ex-

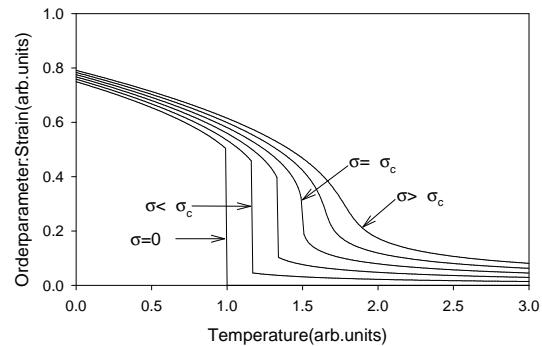


FIG. 1: Prediction for the strain as a function of temperature in a *homogeneous* elastomer under an aligning stress σ .

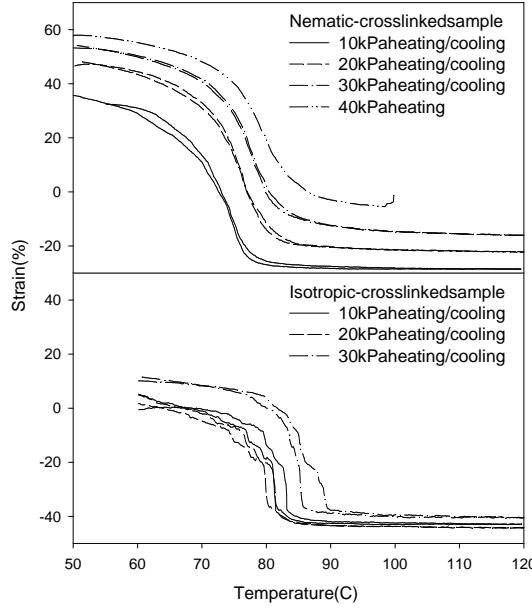


FIG. 2: Data for strain as a function of temperature over a range of applied stress, for elastomers crosslinked in the nematic and isotropic phases. Strain is measured relative to an arbitrary zero value. The nematic-crosslinked sample broke during the 40 kPa heating run.

planation is correct, then one would optimize elastomers for applications by reducing the heterogeneity to get the transition in the narrowest possible range of temperature.

To determine which explanation is correct, we measure the strain as a function of temperature over a range of applied tensile stress. We use elastomer samples crosslinked in the nematic phase, which should have a large internal stress imprinted by the crosslinking process, and samples crosslinked in the isotropic phase, which should not have an internal stress. The samples are composed of a 50/50 mol % mixture of 4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate (MAOC4) and 4'-acryloyloxybutyl 2,5-di(4'-pentylcyclohexyloxy)benzoate (MACC5), with 5 mol % of the 1,6-hexanediol diacrylate crosslinker. Nematic-crosslinked samples are simultaneously polymerized and crosslinked in a cell with rubbed surfaces at 30°C, and isotropic-crosslinked samples at 110°C. Synthesis, preparation, and characterization of nematic-crosslinked samples are described in Ref. [8]. At low temperature those samples have long-range orientational order, with order parameter $S = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$ of 0.3, as determined by polarized FTIR spectroscopy [8].

Under zero applied stress, the samples were seen to extend and contract as a function of temperature. For finite applied stress, the thermoelastic curves for strain vs. temperature were obtained in static measurements on a dynamic mechanical analyzer (TA Instruments DMA 2980) at a heating/cooling rate of 0.5°C/min. The data are shown in Fig. 2. The strain is measured relative to

an arbitrary zero value. These plots show a smooth non-singular isotropic-nematic transition at all values of the applied stress, and under both crosslinking conditions, although the transition is sharper at lower applied stress and under isotropic crosslinking.

To assess whether the data are compatible with the first proposed explanation, we use Landau theory for a homogeneous elastomer. The free energy can be expanded in terms of the orientational order parameter S and the strain e relative to the high-temperature relaxed state. This expansion gives [13]

$$F = \frac{1}{2}\alpha'(T - T_0')S^2 - \frac{1}{3}b'S^3 + \frac{1}{4}c'S^4 - ueS - \sigma e + \frac{1}{2}\mu e^2, \quad (1)$$

where T is the temperature and σ is the effective stress acting on the elastomer, which is a combination of the applied stress and the internal stress due to anisotropic crosslinking. We average this free energy over S to obtain the free energy in terms of e alone,

$$F = \frac{1}{2}\alpha(T - T_0)e^2 - \frac{1}{3}be^3 + \frac{1}{4}ce^4 - \sigma e. \quad (2)$$

Minimizing this free energy over e gives

$$\alpha(T - T_0)e - be^2 + ce^3 - \sigma = 0. \quad (3)$$

This equation implicitly determines e as a function of T and σ . In particular, it predicts a critical point at

$$e_c = \frac{b^3}{27c^2}, \quad T_c = T_0 + \frac{b^2}{3c\alpha}. \quad (4)$$

We attempt to fit the prediction of Eq. (3) to the data presented above. For computational convenience, we solve Eq. (3) for the inverse function $T(e)$ and fit it to temperature as a function of strain. Because this inverse function depends linearly on the fitting parameters, we can use linear regression techniques. Since the strain data are reported relative to an arbitrary zero, we subtract off the high-temperature asymptotic strain from the data to obtain the values of e for the analysis. This procedure fits the data to the functional form shown in Fig. 1. The fit can be on either the first-order or the supercritical side of the critical point, depending on the data.

Our analysis gives the fits shown by the dashed lines in Fig. 3. These fits agree well with the data in the high- and low-temperature limits, but they are unsatisfactory for intermediate temperatures. In all cases, the fitting function shows a first-order discontinuity at the isotropic-nematic transition. Apparently the regression sacrifices the intermediate regime in order to give good fits at high and low temperatures. We also fit the data to an extended model with fifth- and sixth-order terms in the free energy (not shown), and the fits are also unsatisfactory. These results show that the data are not consistent with a supercritical evolution between the isotropic and nematic phases. The high- and low-temperature data do not connect together following the prediction for a supercritical transition in a homogeneous elastomer.

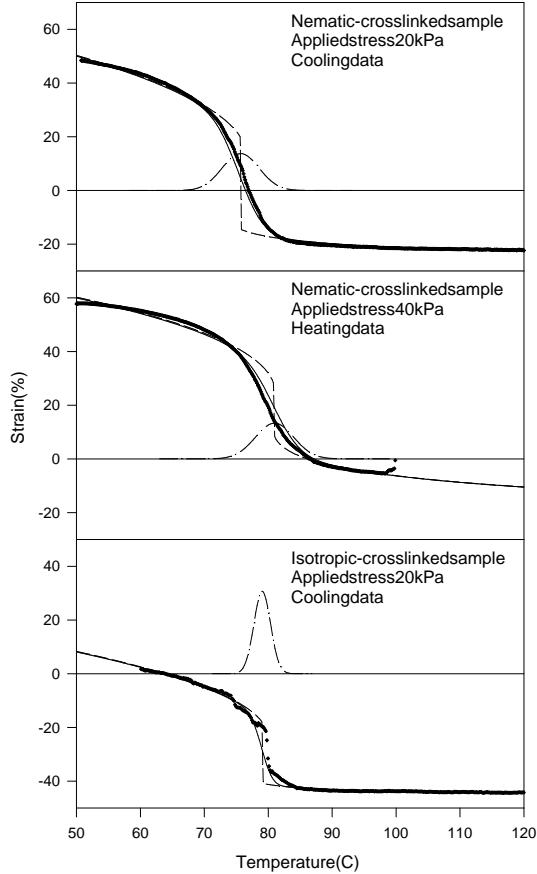


FIG. 3: Fits of selected data sets to the models discussed in the text. Dashed lines: Homogeneous model. Solid lines: Heterogeneous model. Dot-dashed lines: Distribution of the transition temperature T_{NI} in the heterogeneous model.

In addition to the unsatisfactory fits, there are two other indications that the data are inconsistent with predictions for a supercritical transition in a homogeneous elastomer. First, we can use the Landau theory to extract the maximum slope $\partial e / \partial T$ at the inflection point in the supercritical regime $\sigma > \sigma_c$. The result is

$$\left(\frac{\partial e}{\partial T} \right)_{\max} = - \frac{\alpha}{3c^{2/3}(\sigma^{1/3} - \sigma_c^{1/3})}. \quad (5)$$

This equation implies that the maximum slope should decrease inversely with stress $\sigma - \sigma_c$ beyond the critical point. However, the measured slope depends rather weakly on stress, and it is approximately constant with respect to stress at low stress. This result suggests that some mechanism other than supercritical stress is responsible for the observed broadening of the transition. Second, in this experiment we minimize any symmetry-breaking influence on the elastomer by crosslinking one sample in the isotropic phase and reducing the applied stress to 10 kPa. Even under these conditions, the experiment shows a smooth crossover between the isotropic and nematic phases. It is unlikely that these conditions

could give a supercritical stress on the system; it is more plausible that another mechanism is involved.

Because of these inconsistencies between the data and the model for a homogeneous elastomer, we consider a model for heterogeneity in the elastomer. As a hypothesis, we suppose that heterogeneity gives regions with different isotropic-nematic transition temperatures. We consider a Gaussian distribution of the transition temperature T_{NI} , and thus of the parameter T_0 . Hence, the macroscopic strain is an average over the strain of local regions, which can be written as the convolution

$$e_{\text{hetero}}(\sigma, T) = \int d(T_0) e_{\text{homo}}(\sigma, T - T_0) P(T_0), \quad (6)$$

where

$$P(T_0) = \frac{1}{\sqrt{2\pi}T_{0,SD}} \exp \left[-\frac{1}{2} \left(\frac{T_0 - \bar{T}_0}{T_{0,SD}} \right)^2 \right]. \quad (7)$$

To compare this heterogeneous prediction with the data, we take the homogeneous fit discussed above and convolve it with a Gaussian of adjustable width $T_{0,SD}$. We fit the width to the data through a nonlinear least-squares procedure. The results are shown by the solid lines in Fig. 3. The convolution does not change the high- or low-temperature limits of the fits, which were already satisfactory, but it has a great effect on the intermediate-temperature behavior. Instead of a discontinuous jump in the strain at T_{NI} , the fitted curves show a smooth crossover as the elastomer changes from mostly isotropic to mostly nematic. The shape of the curve in the intermediate-temperature regime is approximately an error function of width $T_{0,SD}$. This behavior agrees with the trend in the data. As a result, the heterogeneous model gives good fits over the full range of temperature.

To analyze the fitting results further, we would like to know how close an elastomer is to the critical point at $\sigma = \sigma_c$. For that reason, we define the dimensionless stress ratio σ/σ_c , where σ is the apparent stress that comes from fitting the homogeneous model to the high- and low-temperature data, and $\sigma_c = b^3/(27c^2)$ is the critical stress derived from the parameters b and c in those fits. In Fig. 4(a) we plot the stress ratio for isotropic- and nematic-crosslinked samples vs. applied stress. From this plot, we can make several observations. First, the stress ratio increases linearly with applied stress. This increase is expected, since an applied stress should shift a sample toward the critical point. At the highest applied stress of 40 kPa, the nematic-crosslinked sample nearly reaches the critical point. When the applied stress goes to zero, the stress ratio does not go to zero but rather to a finite limit. This behavior shows that the effective stress acting on a sample is a combination of the applied stress and an internal stress. For the nematic-crosslinked sample, we expect an internal stress due to the anisotropy of the crosslinking, and indeed the internal stress is large, giving a contribution equivalent to 35 kPa of applied stress.

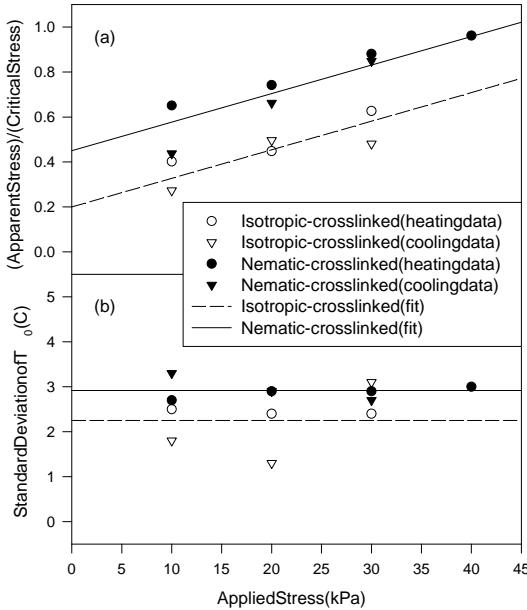


FIG. 4: Analysis of the fitting results for isotropic- and nematic-crosslinked elastomers over a range of applied stress. (a) Stress ratio σ/σ_c , indicating how close an elastomer is to the critical point. (b) Standard deviation $T_{0,SD}$, indicating the width of the distribution of transition temperatures.

For the isotropic-crosslinked sample, we do not expect an internal stress, but Fig. 4(a) implies that some internal stress is present, equivalent to 16 kPa of applied stress. This surprising contribution must come from some unintentional anisotropy in the sample preparation, perhaps related to the boundary conditions on the sample.

Another parameter to extract from the fits is the Gaussian width $T_{0,SD}$ that is required to fit the isotropic-nematic crossover in the data. In Fig. 4(b) we plot $T_{0,SD}$ vs. applied stress for isotropic- and nematic-crosslinked samples. The plot shows that the fitted values of $T_{0,SD}$ have some scatter, but they are not correlated with applied stress. This result is reasonable, because the distribution of transition temperatures should not be related to applied stress. The average value of $T_{0,SD}$ is approximately 2.25°C for the isotropic- and 2.9°C for the nematic-crosslinked sample. This corresponds to a distribution with a full width at half maximum of 5.3°C or 6.8°C in each of the samples, respectively.

As a final point, we note that our model for a distribution of transition temperatures describes only one way in which heterogeneity can affect liquid-crystalline elastomers. A second possible mechanism would be a distribution in the direction of the imprinted orientational order, especially in a sample crosslinked in the nematic phase. Indeed, a distribution of quenched director orientations might explain the greater value of the Gaussian width found in the nematic- than in the isotropic-crosslinked sample. A distribution of transition temper-

atures is random-bond disorder, while a distribution of quenched director orientations is random-field disorder. Our study has shown that the sharpness of the isotropic-nematic transition is controlled by heterogeneity, but it has not addressed the question of whether random-bond or random-field disorder is dominant. Indeed, measurements of the strain vs. temperature may not be enough to make this distinction; more microscopic studies may be needed. This remains a question for future research.

In conclusion, we have developed a phenomenological theory for the isotropic-nematic transition in liquid-crystalline elastomers. This theory is a variation on Landau theory, which allows for quenched disorder in the elastomer through variation in the transition temperature. We compare this theory with measurements of the strain vs. temperature over a range of applied stress, for samples crosslinked in the isotropic and nematic phases. This comparison shows that applied stress, internal stress, and quenched disorder are *all* involved in the shape of the thermoelastic curve. In particular, quenched disorder is a key limiting factor in the sharpness of the isotropic-nematic transition, which must be controlled for applications of liquid-crystalline elastomers.

We thank P. Keller for synthesizing the materials. This work was supported by the Office of Naval Research and the Defense Advanced Research Projects Agency. HGJ was supported by the National Research Council Associateship Program.

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